Photodegradation of Polyethylene Films Formulated with a Titanium-Based Photosensitizer and Titanium Dioxide Pigment

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SYNOPSIS

This work reports on the photodegradation of low-density polyethylene films formulated with titanium (IV) oxide actylacetonate (TAc) and titanium dioxide pigment in different proportions; no previous reports on the photoactivity of this acetylacetonate have been found. Samples of blow-extruded films were submitted to accelerated UV aging with fluorescent lamps and the polymer degradation measured. The changes in carbonyl groups, molecular weight, and film elongation at break are discussed. The results show that TAc can promote photooxidation and accelerate the film degradation. The retention percent of elongation at break (E_B) is apparently proportional to the carbonyl index irrespective of the formulation but has different relations with molecular weight (M_n), time, or the number of chain scissions (n), probably as a result of microstructural differences. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Photodegradable plastics can help to solve the problems of solid polymeric waste,[1] despite the controversy regarding recycling or degradation,[2,3] and their use is more important every day as a result of new environment protection laws. There are two basic routes to design such materials: grafting photosensitive moieties onto the macromolecular chain, during or after the polymerization process, and adding low-molecular-weight chemicals; both routes aim for photooxidation or photodegradation of the polymer. There are a lot of studies[4-7] regarding the use of low-molecular-weight photoactive additives, but polymeric chemicals are also used[8] with different functional groups; good examples of these additives are metal complexes,[9] specifically transition metal acetylacetonates. The photoactivity of these complexes depends on the particular metal; iron compounds are more active than those of cobalt; nickel and zinc do not show photoactive action.[9] Iron and cobalt compounds are prooxidant and prodegradative. Their high ultraviolet activity is apparently related to a low thermal and photochemical stability, as well as to the lack of antioxidant action. No specific reports on titanium acetylacetonates as photoactive additives have been found although their use for fiber sizing is documented.[10] Despite this, it is known that titanium dioxide is a photoactive pigment that can promote photodegradation, or perform like a UV screen, depending on its concentration and crystalline structure: rutile is relatively inactive, while anatase is photoactive and promotes degradation[11-17] specifically on the surface, which may be later eroded in a phenomenon called bleaching.

The general way to determine photoactivity is by measuring changes in any of the three parameters: mechanical properties (mainly tensile tests), carbonyl group evolution, or molecular weight modification. There are studies reporting on each parameter, though those dealing with molecular weight are scarce, and very few analyze simultaneously all of them.[18] Specifically on the UV degradation of polyolefins, possible routes for forming chemical func-

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tional groups, and their role in polymer chain breaking, have been reported[19-25]; on the other hand, data on changes in molecular weight of polyethylene in films, as a function of environmental aging,[26] have been published recently. In this work the photoactive characteristics of titanium (IV) oxide acetylacetonate (TAc) are evaluated in low-density polyethylene (LDPE) films, pigmented with titanium dioxide (rutile) and similar to those used in agriculture; films without additive or pigment are used as a reference. Polymer degradation is characterized by measuring the changes in chemical functional groups by infrared spectrometry (FTIR), the modification of molecular weight distribution by size exclusion chromatography (SEC), and the reduction of maximum elongation of the film by tensile tests. The number of macromolecular chain scissions is calculated using the number-average molecular weight and the relationship reported by David;[26] the results are analyzed looking for correlations.

EXPERIMENTAL

Polymer

Commercial low-density polyethylene (PEMEX PX20020X) was used as received from the supplier. The physical characteristics, determined at our laboratory, are density of 0.921 g/cm^3 (gradient column method ASTM D1505), melt flow index (MFI) of 2.031 $g/10$ min (ASTM D1238, test condition E: 190°C; load 2160 g), and molecular weight averages of $M_n = 75,100$ and $M_w = 134,000$, measured by SEC. Additive. Titanium (IV) oxide acetylacetonate (MW = 262 and melting point 200°C) from Aldrich Chemicals was used as received.

Pigment

Titanium dioxide (TiO_2) was used as pigment; its principal crystalline structure, determined by X-ray diffraction, is rutile. The X-ray equipment was a Phillips diffractometer PW 1710 with vertical goniometer; the following analysis conditions were used: radiation $CuK\alpha = 0.154$ nm; power of 40 Kv, 50 mA; and scanning rate of 0.5 $2\theta/s$.

Film Preparation

Master batches of TAc (6 wt %) and TiO_2 (30 wt %) were prepared in a laboratory internal mixer (Brabender PL 2000), using CAM rotors at 30 rpm; the temperature was maintained at 160°C. Later they were mixed with virgin polyethylene to obtain

the formulations shown in Table I. Films from these formulations were prepared in a Betol blow-extruder model 32/25, equipped with a screw of $L/D = 25 : 1$ (compression ratio 4 : 1). The temperature profile for the barrel (four zones) was 150, 180, 205, and 210°C; and for the die (two zones) 210 and 210°C. The blowing-extrusion parameters were adjusted to produce films with blow ratio of 2.0 and ca. 40 μm thickness. From these films, samples of 10 × 5 cm were cut and used for ultraviolet aging.

Ultraviolet Accelerated Tests

The film samples were placed in an accelerated aging UV chamber and specimens taken approximately every 12 h to measure degradation. The aging chamber (CIQA constructed) has similar design to those of the Institute of Science and Technology (ICyT) of Madrid, consisting of eight fluorescent lamps (maximum wavelength at 313 nm) and rotating holder for samples; the temperature was 60 ± 1°C. Data acquired during different seasons,[27] for several thickness and type of polyethylene films, suggest that one day of exposure within the chamber is approximately equivalent to one month of environmental aging at the Saltillo, Mexico, region (North latitude 25.25°).

Film Evaluation

Chemical Changes

Carbonyl group evolution was measured in a FTIR (Nicolet 710) analyzing the signal between 1300 and

Table I. Formulation Codes and Concentrations, Used to Prepare the Films for UV Degradation

Additive	Sample Code	Concentration (mmol/100 g PE)	
		TAc	TiO_2
No additive	PE	0.0	
Titanium (IV) oxide acetylacetonate	TAc1	1.0	
Titanium (IV) oxide acetylacetonate	TAc4	4.0	
Titanium (IV) oxide acetylacetonate + titanium dioxide	TAcT1	4.0 + 19.6	
Titanium (IV) oxide acetylacetonate + titanium dioxide	TAcT5	4.0 + 82.2	
Titanium dioxide	$TiO_2$1		19.6
Titanium dioxide	$TiO_2$5		82.2

1800 cm^{-1}, a carbonyl index[7,28] (CI) defined as the ratio of the absorbance (A) at two different wave numbers:

$$CI = A_{1710}/A_{1380} \qquad (1)$$

was used to compare the photoactivity of the different formulations.

Molecular Weight Distributions (MWD)

Molecular weight characteristics of selected samples were obtained in a SEC (Waters 150-C) with refractive index detector and three Ultra Styragel columns, nominal porosity of 10^6, 10^4 Å, and lineal. The solvent was 1,2,4 trichlorobenzene at 140°C and 1 mL/min flow rate. Molecular weight averages were calculated using a universal calibration curve constructed with narrow MWD polystyrene standards, and the respective Mark–Houwink parameters.

The values of number-average molecular weight

(M_n) can be used[26] to calculate the number of chain scissions (n) according to Eq. (2):

$$n = (M_{n,0}/M_{n,t}) - 1 \qquad (2)$$

where $M_{n,0}$ is the initial molecular weight, and $M_{n,t}$ that at time t.

Mechanical Properties

Tensile tests were carried out with an Instron 1122 tensilometer according to the conditions in ASTM D-882 (1 × 10 cm specimens; $T = 23 \pm 2°C$; and crosshead separation speed 200 mm/min). The percent of retention on elongation (E_B) was used to compare the performance of the formulations.

RESULTS AND DISCUSSION

Results of carbonyl index and elongation (retention percent) for all the samples are quoted in Table II.

Table II.   Carbonyl Index and Elongation (Percent of Retention) Change with UV Exposure Time

Sample	$t_{exp.}$ (h)	CI	E_B (% Ret.)	Sample	$t_{exp.}$ (h)	CI	E_B (% Ret.)
PE	0	0	100	TAcT1	48	0.7074	32
PE	12	0.3784	102	TAcT1	60	1.1406	16
PE	24	0.2493	93	TAcT1	86	1.3419	5
PE	36	0.4029	85	TAcT5	0	0	100
PE	48	0.5033	67	TAcT5	12	0.3303	75
PE	60	0.5698	46	TAcT5	24	0.4316	82
PE	99	1.2115	15	TAcT5	36	0.6647	51
PE	112	1.2754	12	TAcT5	42	0.6909	41
TAc1	0	0	100	TAcT5	48	0.7307	67
TAc1	12	0.4948	87	TAcT5	60	0.7754	31
TAc1	24	0.3843	85	TAcT5	86	1.1209	16
TAc1	36	0.6795	41	TiO$_2$1	0	0	100
TAc1	48	0.9655	17	TiO$_2$1	12	0.2519	87
TAc1	60	0.8623	19	TiO$_2$1	24	0.3148	86
TAc1	86	1.3965	4	TiO$_2$1	36	0.1057	84
TAc1	99	1.7215	3	TiO$_2$1	48	0.4939	67
TAc4	0	0	100	TiO$_2$1	60	0.6403	61
TAc4	12	0	71	TiO$_2$1	86	0.8119	28
TAc4	24	0.5901	65	TiO$_2$1	112	1.1872	11
TAc4	36	—	14	TiO$_2$5	0	0	100
TAc4	60	1.1453	9	TiO$_2$5	12	0.3336	85
TAc4	86	1.6283	4	TiO$_2$5	24	—	78
TAc4	99	2.1699	1	TiO$_2$5	36	0.4160	69
TAcT1	0	0	100	TiO$_2$5	48	0.4374	71
TAcT1	12	0.3525	78	TiO$_2$5	60	0.6117	53
TAcT1	24	0.5370	68	TiO$_2$5	86	0.8401	24
TAcT1	36	0.6426	31	TiO$_2$5	112	1.0393	20
TAcT1	42	0.7987	24				

Table III.   Data of the Three Parameters, Measured During UV Exposure, for Selected Samples

Sample Code	$t_{exp.}$ (h)	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	n	CI	E_B (% Ret.)
PE	0	75.2	134	0.00	0.000	100
PE	12	76.9	184	−0.02	0.3784	102
PE	36	54.5	78.5	0.32	0.4029	85
PE	60	41.8	70.6	0.80	0.5698	46
PE	99	29.3	40.9	1.56	1.2115	15
Tac1	24	65.5	219	0.15	0.3843	85
TAc1	36	51.8	154	0.45	0.6795	41
TAc1	60	41.4	57	0.81	0.8623	19
TAc4	12	70.3	125	0.07	0.000	71
TAc4	24	63.8	114	0.18	0.5901	65
TAc4	36	50.5	111	0.49	0.9757	14
TAcT1	24	60.7	171	0.24	0.4370	68
TAcT1	36	44.7	65.8	0.68	0.6426	31
TAcT5	24	62.7	119	0.20	0.4316	82
TAcT5	42	49.7	75.6	0.51	0.6909	40
TAcT5	60	45.4	70.6	0.66	0.7754	31
$TiO_2$1	12	73.0	158	0.03	0.2519	87
$TiO_2$1	36	64.2	189	0.17	0.4057	84
$TiO_2$1	86	41.4	56.1	0.81	0.8119	28
$TiO_2$5	24	64.5	141	0.16	—	77
$TiO_2$5	36	63.0	106	0.19	0.4160	69
$TiO_2$5	60	55.8	88.6	0.35	0.6117	53

The three parameters (CI, E_B, and molecular weight) measured and the calculated number of scissions for selected samples are shown in Table III.

Changes in Carbonyl Index with Time of UV Exposure

Carbonyl indexes (CI) calculated with Eq. (1), for polyethylene (PE) and formulated films, are plotted (Fig. 1) against the squared time of exposure.[29] At short times ($t \leq 12$ h) a sharp increase of CI from zero to approximately 0.25 is observed; later there is a linear change whose slope (1.36 for PE) depends on the TAc and TiO_2 concentration; the highest value (2.92) is for the sample containing 4 mmol TAc/100 g PE (TAc 4). These results suggest that titanium (IV) oxide acetylacetonate accelerates the carbonyl formation, that is, behaves like a prooxidant. When only TiO_2 is used in the formulation, the CI values are lower than those of the polyethylene, suggesting a small stabilizing effect for this pigment. The slopes in this case are 0.84 for 1 mmol TAc/100 g PE and 0.85 for 4 mmol TAc/100 g PE. Considering the low photoactivity reported for rutile titanium dioxide, these results are not surprising. The samples formulated with both TAc (4.0 mmol) and TiO_2 (TAcT1 and TAcT5) fall within the lines

for PE and TAc4, evidencing the antagonistic effect of these compounds.

Molecular Weight Changes with Exposure Time

The changes in molecular weight promoted during the UV aging can be associated with the breaking and recombination process of chain molecules. A lowering of molecular weight is expected when breaking is the main event, while if recombination dominates, branching and eventually gel formation should take place.

Changes in molecular weight averages (M_n and M_w) can be correlated[26,30] with the fraction of broken units in the main chain (p_0) and the fraction of crosslinked units (q_0) obtaining that: if $p_0/q_0 > \frac{1}{2}$, M_n decreases, and if $p_0/q_0 < \frac{1}{2}$, M_n increases; on the other hand, M_w decreases if $p_0/q_0 > 2$ and increases if $p_0/q_0 < 2$.

In Figures 2 and 3 the number- (M_n) and weight- (M_w) average molecular weights are plotted, respectively, against the squared time of exposure. Number-average molecular weight always decreases rapidly at short times of UV exposure ($t < 60$ h) with a tendency to level off later. The samples formulated only with TiO_2 behave in a similar way but show higher values of M_n for same exposure time;

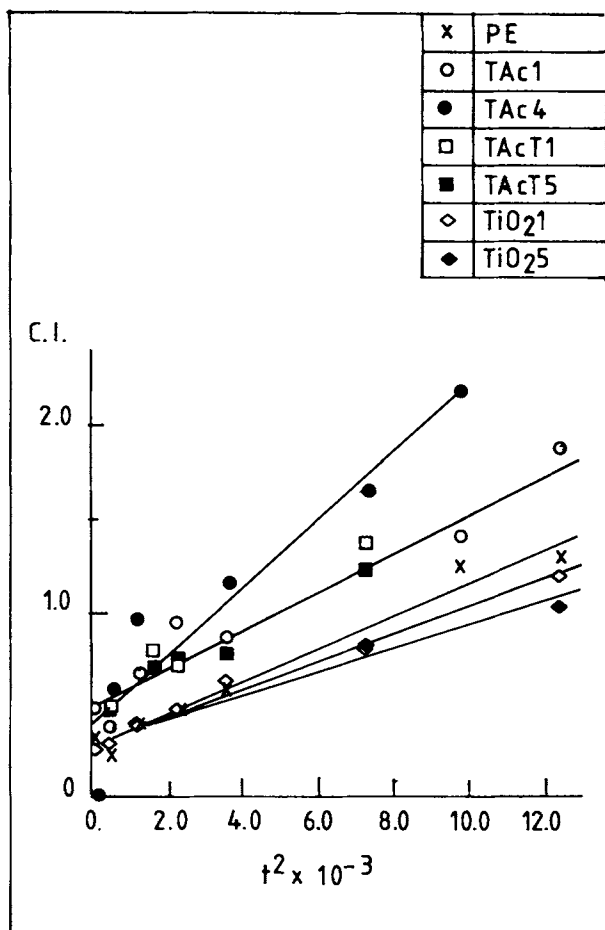| x	PE
○	TAc1
●	TAc4
□	TAcT1
■	TAcT5
◇	TiO$_2$1
◆	TiO$_2$5

C.I.

$t^2 \times 10^{-3}$

Figure 1 Carbonyl index evolution as a function of time to UV exposure.

this is also evidence of the stabilizing role of TiO$_2$ in the system. With regard to M_w; it increases during the first 24 h of exposure but does not reach the gel point, as the samples remain soluble, followed by a sharp decrease (24 < t < 60 h), and leveling off afterward; the sample with TiO$_2$ has only a small increment, but later its M_w is higher than that of PE; finally, the samples TAc4 and TAcT5 do not show this increment.

The results suggest that molecular recombination dominates at short times and thus $2 > p_0/q_0 > \frac{1}{2}$; except in the case of 4 mmol of TAc where both averages diminish all the time. On the other hand, the polymer solubility and the reduction of M_w indicate a higher probability for main chain scission at long times with p_0/q_0 higher than 2; in the sample with the high TiO$_2$ concentration, apparently the chain breaking process is less effective.

The number of average scissions per chain (n) was calculated using M_n and Eq. (2), and show a lineal increment of n with the square of exposure time (Fig. 4). All the samples formulated with TAc

could be fitted to one line, whose slope (3.54×10^{-4}) is higher than that of PE (2.29×10^{-4}), suggesting a slight photodegradative action of TAc. The slope of the line for the samples formulated with TiO$_2$ is 1.025×10^{-4}, evidencing its stabilizing effect.

Tensile Properties Changes

The retention percent of elongation at break (E_B) shows a great dependence of the formulation when plotted against t (Fig. 5); a faster decrease in elongation is observed as the TAc concentration increases; the stabilizing effect of TiO$_2$ is also evident in this plot. As in the other plots, the samples formulated with both compounds lie in between the lines for PE and TAc4.

Relations between Carbonyl Index and Molecular Weight

Carbonyl groups can promote chain scission[20] and consequently reduce the molecular weight; Figure 6
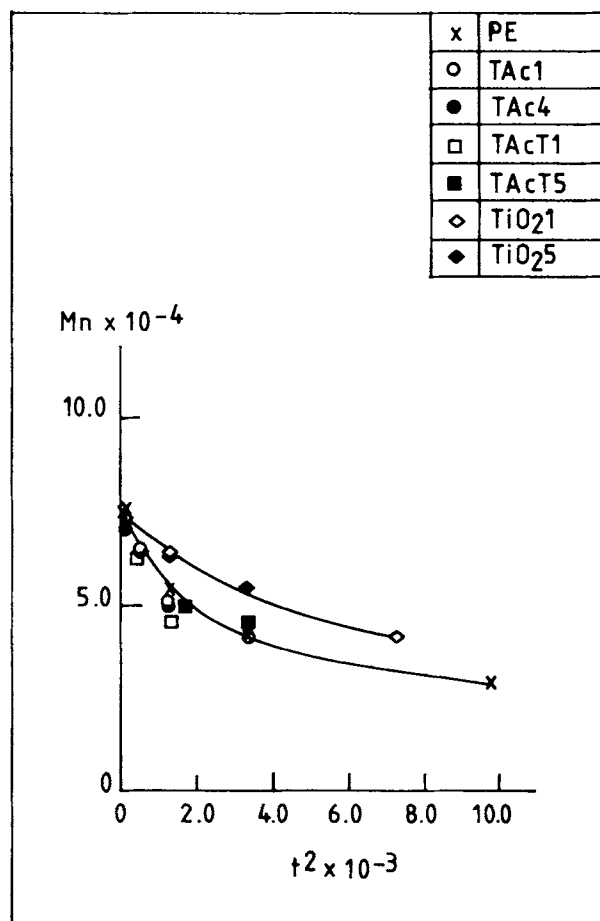

x	PE
○	TAc1
●	TAc4
□	TAcT1
■	TAcT5
◇	TiO$_2$1
◆	TiO$_2$5

$M_n \times 10^{-4}$

$t^2 \times 10^{-3}$

Figure 2 Reduction of molecular weight (M_n) with exposure time to UV irradiation.

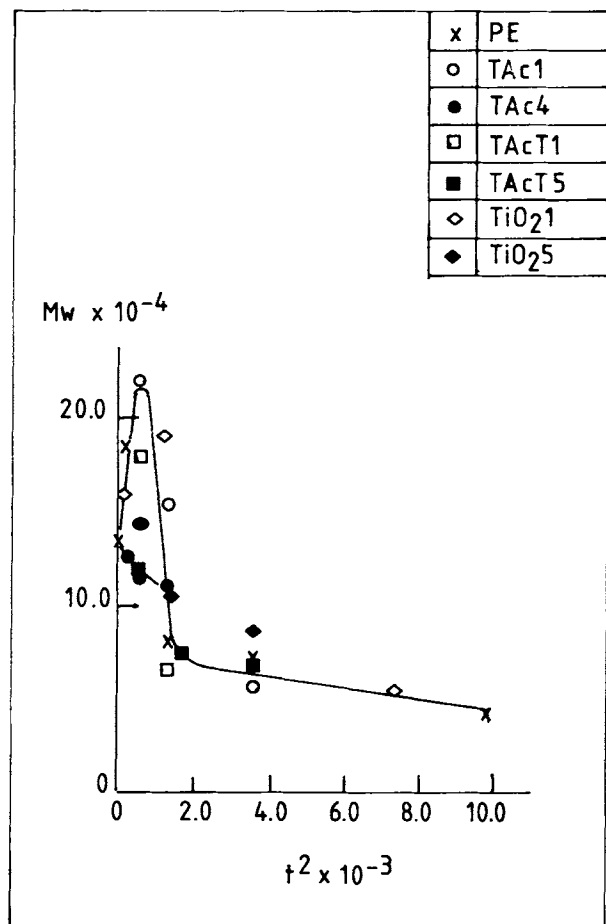| x	PE
o	TAc1
●	TAc4
□	TAcT1
■	TAcT5
◇	TiO₂1
◆	TiO₂5

Figure 3 Changes in molecular weight (M_w) with exposure time to UV irradiation.

shows the CI–M_n plot. The polyethylene without additives shows an apparent induction period where there is carbonyl formation, but no molecular weight reduction. Later there is a steep M_n reduction (0.39 < CI < 0.60). The sample TAc4 shows a steady increase in carbonyl groups with only a slight change of molecular weight. This behavior supports the previous proposition that TAc is mainly a prooxidant. The rest of the samples lie in between these two lines.

In regard to the number of chain scissions and carbonyl index, Figure 7 presents the n^2 vs. CI plot. The PE sample shows the previously mentioned time of induction followed by a lineal change (when the carbonyl index is greater than 0.366) with the following equation:

$$n^2 = 2.881 \quad CI - 1.044 \qquad (3)$$

The samples formulated with TAc, first increase in CI with very few chain scissions (less than 0.5); afterward chain breaking begins to take place gen-

erating lines apparently parallel to that of PE. The effect of TAc or TiO₂ concentration is the same as observed with the other parameters.

Elongation, Carbonyl Groups, and Molecular Weight

Elongation and molecular weight for a polymer chain can be correlated[31] by means of Eq. (4):

$$x = (f/3KT)h \qquad (4)$$

where x is the mean projection of the chain length on the direction of the external (applied) force, f is the mean elastic force, and h the macromolecular chain end-to-end distance, which is proportional to the molecular weight.

The effect of branching on x can be analyzed better by using the radius of gyration (s):
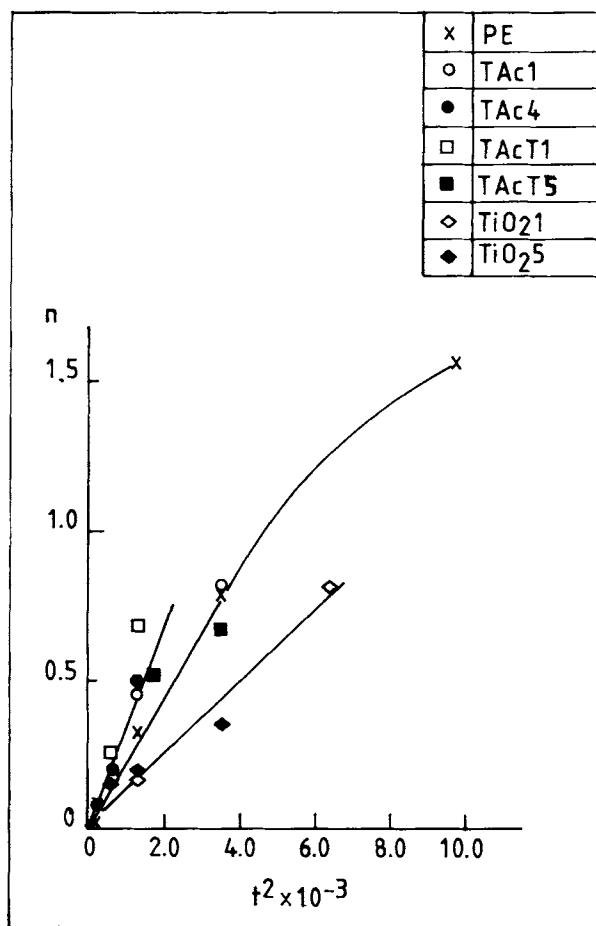
$$s = h/6 \qquad (5)$$

x	PE
o	TAc1
●	TAc4
□	TAcT1
■	TAcT5
◇	TiO₂1
◆	TiO₂5

Figure 4 Increment of main chain scissions (n) with exposure time to UV irradiation.

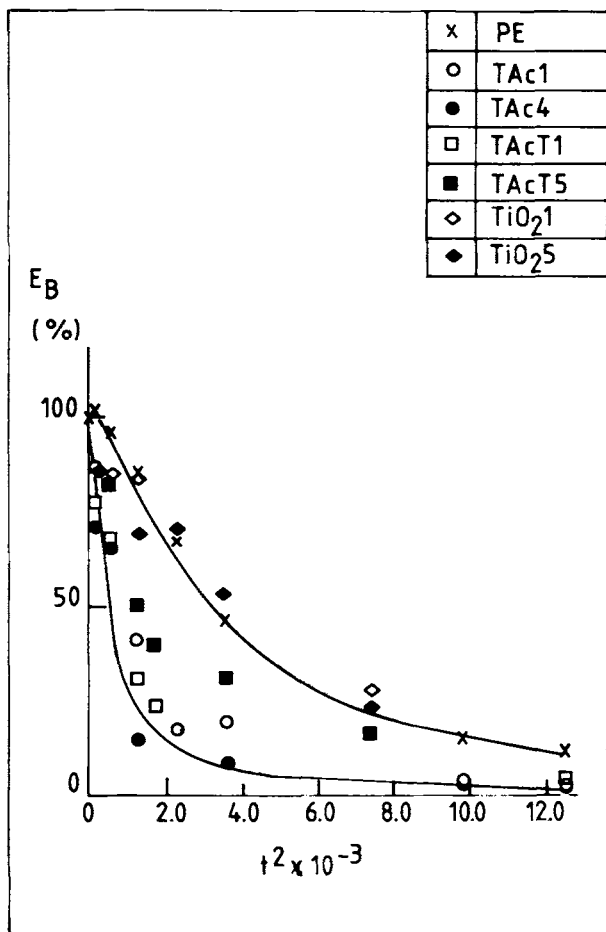| x	PE
○	TAc1
●	TAc4
□	TAcT1
■	TAcT5
◇	TiO$_2$1
◆	TiO$_2$5

Figure 5   Reduction of elongation at break, retention percent, with exposure time.

instead of h. Branching reduces s (if molecular weight is kept constant) and consequently will reduce x. Even more, the introduction of polar groups modifies the radius of gyration and will affect elongation.

When the results of retention of maximum elongation for the samples at different exposure times are plotted against M_n, three lines are found (Fig. 8), that is, for a given value of M_n there are different possible values of E_B. Considering the previous discussion about the relation between elongation, molecular weight, and branching, this behavior is very probably due to differences in chain microstructure branching and carbonyl groups. This strongly suggests that the scission–recombination events, promoting defects, are modified by the presence of TAc.

On the other hand the E_B data for all samples fall on one single curve (Fig. 9) when plotted against the squared carbonyl index, despite all differences observed previously. This behavior is quite interesting because it suggests that the elongation retention in these samples is mainly defined by the mo-

lecular size (radius of gyration), which in this particular case depends on chain rupture leading to branching and functional groups formation. In agreement with the reported photooxidation mechanisms[20,32,33] these events are quite probable during photodegradation:
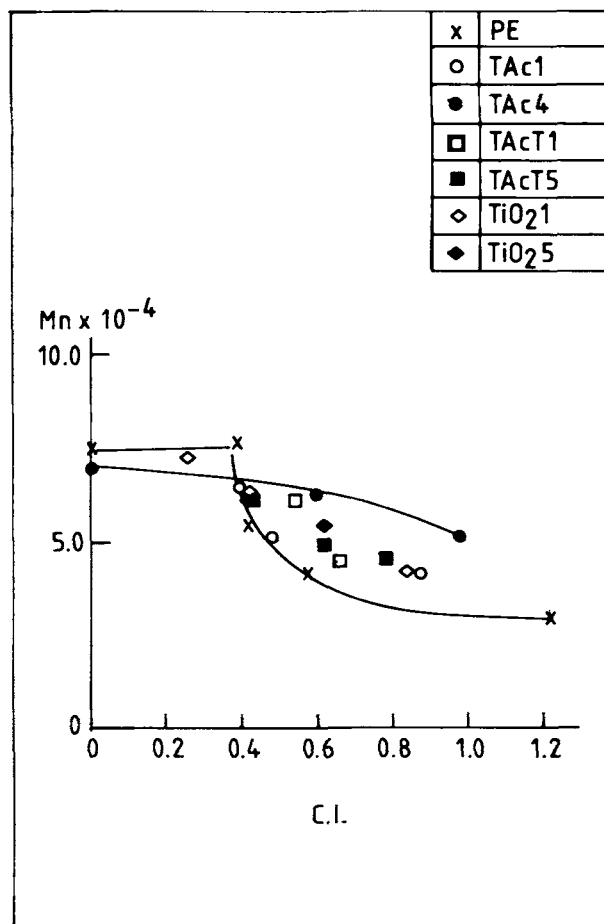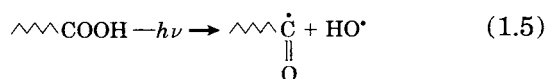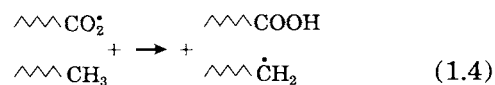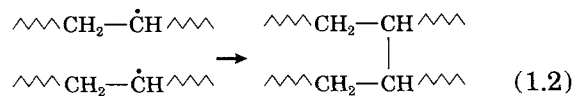
$$\text{/\/\/\ } CH_2\text{—}CH_2\text{/\/\/\ } —h\nu \rightarrow \begin{array}{l} \text{/\/\/\ }\dot{C}H_2 + \text{/\/\/\ }\dot{C}H_2 \\ \text{/\/\/\ }CH_2\text{—}\dot{C}H\text{/\/\/\ } + \dot{H} \end{array}$$

$$(1.1)$$

$$\begin{array}{l} \text{/\/\/\ }CH_2\text{—}\dot{C}H\text{/\/\/\ } \\ \rightarrow \\ \text{/\/\/\ }CH_2\text{—}\dot{C}H\text{/\/\/\ } \end{array} \quad \begin{array}{l} \text{/\/\/\ }CH_2\text{—}CH\text{/\/\/\ } \\ | \\ \text{/\/\/\ }CH_2\text{—}CH\text{/\/\/\ } \end{array} \quad (1.2)$$

$$\text{/\/\/\ }\dot{C}H_2 + O_2 \rightarrow \text{/\/\/\ }CO_2^\bullet \qquad (1.3)$$

$$\begin{array}{l} \text{/\/\/\ }CO_2^\bullet \\ + \\ \text{/\/\/\ }CH_3 \end{array} \rightarrow \begin{array}{l} \text{/\/\/\ }COOH \\ + \\ \text{/\/\/\ }\dot{C}H_2 \end{array} \qquad (1.4)$$

$$\text{/\/\/\ }COOH —h\nu \rightarrow \text{/\/\/\ }\underset{\underset{O}{\|}}{\dot{C}} + HO^\bullet \qquad (1.5)$$

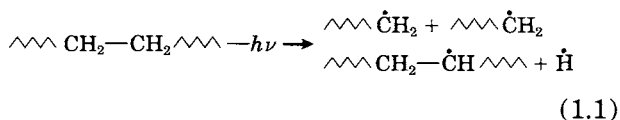| x	PE
○	TAc1
●	TAc4
□	TAcT1
■	TAcT5
◇	TiO$_2$1
◆	TiO$_2$5

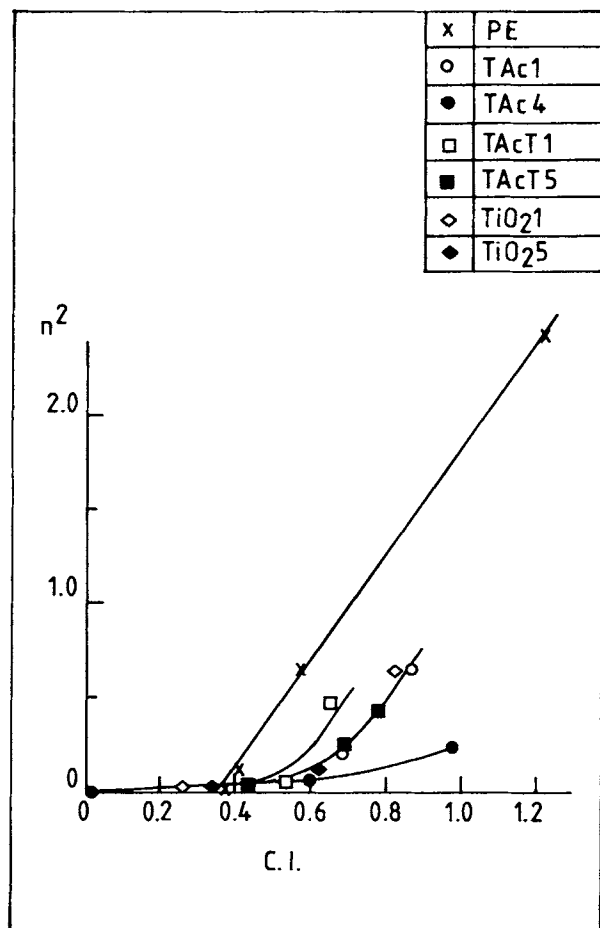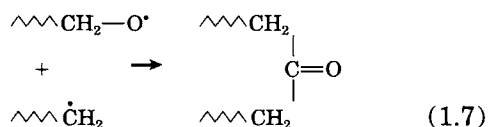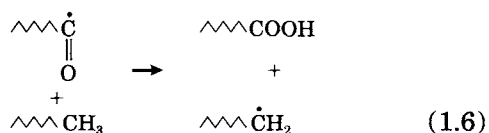**Figure 6**   Relation between molecular weight (M_n) and carbonyl index.

Figure 7 Relation between the number of chain scissions (n) and carbonyl index.

$$
\begin{array}{ccc}
\wedge\!\wedge\!\wedge\overset{\bullet}{\underset{\parallel}{C}} & \wedge\!\wedge\!\wedge COOH & \\
\quad O & \rightarrow & + \\
\quad + & & \\
\wedge\!\wedge\!\wedge CH_3 & \wedge\!\wedge\!\wedge \overset{\bullet}{C}H_2 & (1.6)
\end{array}
$$

$$
\begin{array}{ccc}
\wedge\!\wedge\!\wedge CH_2{-}O^{\bullet} & \wedge\!\wedge\!\wedge CH_2 & \\
\quad + & \rightarrow & \underset{\mid}{C}{=}O \\
\wedge\!\wedge\!\wedge \overset{\bullet}{C}H_2 & \wedge\!\wedge\!\wedge CH_2 & (1.7)
\end{array}
$$

where $\wedge\!\wedge\!\wedge$ represent a polymer chain segment. The results suggest that the carbonyl index is a better parameter (better than M_n or time alone) to evaluate the overall process of photodegradation in TAc-sensitized polyethylene, possibly due to the prooxidant action of the additive. However, the clear establishment of the preferential degradation path in the photodegradation process, and the TAc action mechanism, requires not only the measurement of the molecular weight and functional groups but also

the branching characteristics, identification of the intermediate molecular species, and kinetic data.

CONCLUSIONS

Titanium (IV) oxide acetylacetonate (TAc) behaves as a prooxidant in the accelerated UV photodegradation of polyethylene, in a similar way to other transition metal acetylacetonates.

The titanium dioxide used as pigment in the formulations has a slight stabilizing effect on the system.

Apparently the microstructure of polyethylene molecules degraded with TAc, is different from those PE molecules degraded without the acetylacetonate. The results suggest, for the same molecular weight species, a higher carbonyl content and possibly degree of branching, in the case of macromolecular chains degraded with titanium (IV) oxide acetylacetonate.
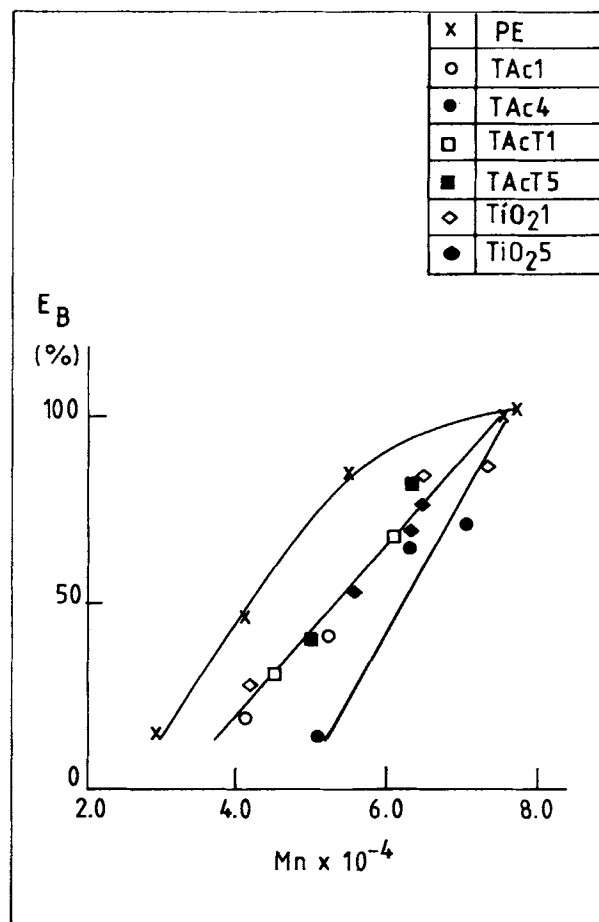

Figure 8 Relation between elongation at break and molecular weight.

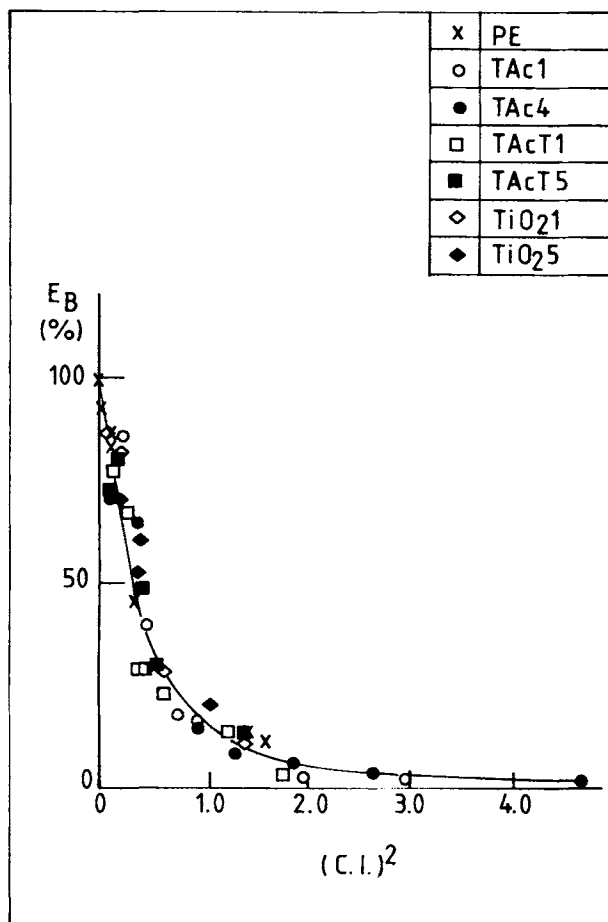| X | PE |
o	TAc1
●	TAc4
□	TAcT1
■	TAcT5
◇	TiO₂1
◆	TiO₂5

Figure 9 Single relation between elongation at break and carbonyl index for all formulations.

Molecular weight results suggests that there is some chain recombination at short exposure times, except for the film with the highest TAc concentration. These results show also that the number of chain scissions is higher for the samples formulated with TAc than those of PE, when similar exposure times are compared.

It was possible to fit the elongation percent retention of all samples to one line when plotted against the squared value of the carbonyl index; all other variables depend on the particular formulation. This behavior could be related to the relationship between the elongation and molecule size, the last depending on functional groups and branching, and suggest a good accounting of these parameters by the carbonyl index.

There is a reduction of the exposure time required to reach a 50% loss in elongation at break, depending on TAc and titanium dioxide concentrations. This effect and the high content of carbonyl groups, pro-

moted by TAc, may be of some use to design photodegradable films.

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